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Photostability of hydrophobic amides of pyridinecarboxylic acid as copper extractants from chloride media

Aleksandra Borowiak-Resterna, Karolina Klonowska [*],
Andrzej Olszanowski, Marta Tomaszewska

Institute of Chemical Technology and Engineering, Poznań University of Technology, Pl. Skłodowskiej-Curie 2, 60-965 Poznań, Poland

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Abstract

The photostability of *N*-alkyl and *N,N*-dialkylpyridine-3-carboxamide, and *N*-alkyl and *N,N*-dialkylpyridine-2-carboxamide, and their copper complexes were studied. The obtained results indicated the influence of light (UV and vis) on the stability of pyridinecarboxamides. The degree of photodegradation depended on the type of solvent, the presence of water, hydrochloric acid or air in the solution. Also, the structure of compounds (the number and position of the amides group, structure of the amides carbon chain) influenced amides photostability. Products of photofragmentation of amides groups and photosubstitution at the pyridine ring were identified. Influence of ions of copper(II) and chloride during the photodegradation of copper complexes with pyridinecarboxamide was analyzed.

Keywords: Photostability; Copper complexes; Pyridinecarboxamide; UV–vis; Photosubstitution

1. Introduction

Copper(II) chloride can form complexes with pyridine and its derivatives in water, ethanol and aprotic solvents [1,2]. Pyridine derivatives with electron-attracting substituents in the ring, which are weak basic organic compounds, are used to transfer copper(II) ions from the chloride media to organic solutions. Esters and amides of pyridinemono- and dicarboxylic acids have been proposed by ZENECA (early ICI) for copper extraction from concentrated chloride solutions [3]. Equilibrium studies of extraction for hydrophobic pyridinemonocarboxamides show that these compounds are stronger copper(II) extractants from chloride solutions at pH >3 than pyridinecarboxylic acid esters [4]. The extraction abilities of pyridinecarboxamides depend on the structure, position and number of amide groups in the pyridine ring. Amides with one alkyl group are stronger extractants than amides with two alkyl chains. However, these “strong” extractants and their complexes with copper(II) are slightly dissolved in hydrocarbon diluents. Pyridinecarboxamides with *N,N*-dialkylamide groups are well soluble in organic solvents.

It was found that during the copper(II) extraction from chloride solutions, in the presence of amide excess, *N*-alkylpyridine-3-carboxamides form $CuCl_2L_2$ complexes (L-ligand), though *N,N*-dialkylpyridine-3-carboxamides can form two complexes $CuCl_2L_2$ or $CuCl_2L_3$ [4,5].

The resistance of the extractants to light is important during industrial extraction processes when extraction and stripping are carried out in installations with open mixers and settlers in countries where exposure to light is unavoidable. Previous studies indicated that hydroxyoxime extractants degraded on exposure to light and the rate of photodegradation was influenced by temperature, the presence of water and sulphuric acid [6–8]. Earlier works have shown that hydrophobic esters of pyridinecarboxylic acids and their copper-complexes degraded under exposure to light [9]. The influence of solvent type was also observed. Diester degraded faster than mono-ester with the analogy group. Increase of photodegradation caused the presence of 2-ethylhexyl groups. Also, the presence of hydrochloride acid and water influenced the stability of esters. The photodegradation of extractants and their copper-complexes confirmed the impact of Cu^{2+} and Cl^{-} on the rate of photoreaction.

The photoreactivity of pyridinecarboxamides (picolinamide, nicotinamide and isonicotinamide) in alcohol and alcohol–acid

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[*] Corresponding author. Tel.: +48 616653688; fax: +48 616653649.
E-mail address: Karolina.Klonowska@put.poznan.pl (K. Klonowska).

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solutions were studied [10,11]. In alcoholic solution, these compounds undergo photosubstitution (alkoxylation, hydroxyalkylation and alkylation at pyridine ring) and photodegradation. The methylation of pyridine-3-carboxamide in the presence of mineral acid occurs effectively at lower concentrations of acid but metoxylation can be observed only in higher concentrations of acid. The alkylation of pyridine-2-carboxamide was indicated at only four position.

The aim of this work was to study the photostability of *N*-alkyl and *N*,*N*-dialkylpyridine-3-carboxamides and *N*-alkyl and *N*,*N*-dialkylpyridine-2-carboxamides: *N*-dodecylpyridine-3-carboxamide **1**, *N*-(2-ethylhexyl)pyridine-3-carboxamide **2**, *N*,*N*-dihexylpyridine-3-carboxamide **3**, *N*,*N*-dibutylpyridine-3-carboxamide **4**, *N*-dodecylpyridine-2-carboxamide **5**, *N*-(2-ethylhexyl)pyridine-2-carboxamide **6** and *N*,*N*-dihexylpyridine-2-carboxamide **7**, as the model extractants of copper from chloride media. The research was carried out in organic solvent (toluene, octane and a mixture of octane–toluene), using UV–vis and vis radiation. The influence of water, hydrochloric acid or air and the effect of the copper(II) ion on the stability of the amides under light exposure were measured.

2. Experimental

Synthesis of pyridine-3 (and -2)-carboxamides synthesized and characterized as reported previously [4]. A purity of 98-99% for synthesized amides was determined by GC/MS. UV, FT/IR, ^{1}H and ^{13}C NMR, and MS spectra proved the structure of the obtained compounds.

Complexes of pyridine-3-carboxamides with copper(II) were obtained in an extraction process. Studies were performed at constant extractant concentration equal to 2×10^{-1} mol L^{-1} in toluene. The phase volume ratio was 1. The compositions of the aqueous phase are given in Table 1. After extraction the concentration of copper complexes in the toluene phase was $5–9 \times 10^{-3}$ mol L^{-1} for Cu1 and Cu3 complexes, and $1–2 \times 10^{-1}$ mol L^{-1} for Cu2 and Cu4 complexes. Vis spectra of copper complexes with amide in toluene: *N*-(2-ethylhexyl)pyridine-3-carboxamide λ_{max} $(\varepsilon) = 688$ (13.8) for Cu1 and Cu3; *N*,*N*-dihexylpyridine-3-carboxamide λ_{max} $(\varepsilon) = 774–776$, ∼850 nm (129) for Cu1 and Cu3, 858 (121) for Cu2 and 860 (127) for Cu4; *N*,*N*-dibutylpyridine-3-carboxamide λ_{max} $(\varepsilon) = 788$ (137) for Cu1 and Cu3, 860 (221) for Cu2 and 868 (285) for Cu4 [5].

Table 1
Compositions of the aqueous phase in the extraction process (extractant concentration: 2×10^{-1} mol L^{-1} in toluene; the phase volume ratio was 1)

Solution	Concentration (mol L^{-1})	
	LiCl	CuCl$_2$
Cu1	4	1×10^{-2}
Cu2	4	1
Cu3	6	1×10^{-2}
Cu4	6	1

2.1. Photodegradation procedure

Photodegradation was carried in the same way as with other derivatives of pyridinecarboxylic acid [12], individual model hydroxyoximes and commercial hydroxyoxime extractants [6–8].

The amides samples, 1×10^{-3} mol L^{-1} in octane, toluene and a mixture of octane–toluene (4:1, v/v) were exposed in a Heraeus photoreactor of 120 mL volume, containing a mercury medium pressure lamp TQ 150 W (Heraeus) and optical filter (quartz or duran glass). The lamp was positioned within the inner part of the photoreactor and cooling water was circulated through a Pyrex jacket surrounding the tube. The quantum yield of the lamp in the photoreactor was 7.86×10^{-5} Einstein dm^{-3} min^{-1}. In some experiments, water or hydrochloric acid (4 mol L^{-1}) was also added to 5% of volume to the solutions of octane–toluene or toluene. The solutions were irradiated under bubbling argon or air with the stationary flow of 2 cm^3 min^{-1} at 20–23 °C.

Analyses of solutions after light exposure were done using a HPLC/UV with a diode array detector. For the identification of the photoproducts the HPLC/MS technique was also applied using a Waters-Micromass HPLC with an electrospray ionization detector.

The toluene solutions of copper complexes of pyridine-3-carboxamide, Cu1–Cu4 (1×10^{-3} mol L^{-1} of ligand concentration) were exposed for 30–240 min in the same manner as amides. The content of the amide in the organic phase after photodegradation was measured using the HPLC technique. Copper stripping was carried out with water, and the content of the extractant in the toluene phase was measured.

3. Results and discussion

The obtained results of photodegradation of the pyridinecarboxamides in octane, toluene, an octane–toluene solution and with 5% (v/v) water or hydrochloric acid in toluene or an octane–toluene solution, indicated that all the tested amides degraded under exposure to UV–vis light. The least degree of photodegradation of *N*-dodecylpyridine-3-carboxamide is observed in toluene solutions, slightly faster photodegradation occurred in the mixture of octane–toluene and in the octane solu-

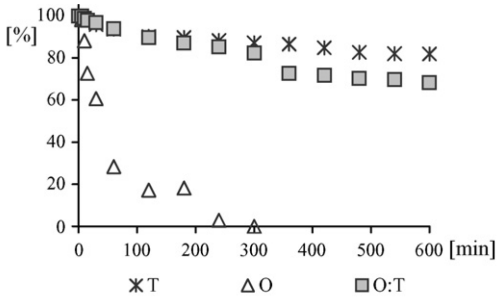


Fig. 1. Relative contents of non-degraded *N*-dodecylpyridine-3-carboxamide dissolved in octane O, toluene T and an octane–toluene solution O:T during exposition of UV–vis light in an argon atmosphere.

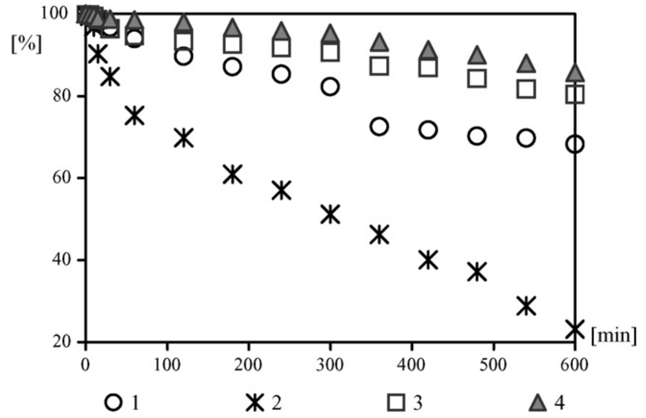


Fig. 2. Relative contents of non-degraded *N*-dodecylpyridine-3-carboxamide **1**, *N*-(2-ethylhexyl)pyridine-3-carboxamide **2**, *N,N*-dihexylpyridine-3-carboxamide **3**, *N,N*-dibutylpyridine-3-carboxamide **4**, dissolved in a mixture of octane–toluene (4:1, v/v) during photodegradation (UV–vis, argon).

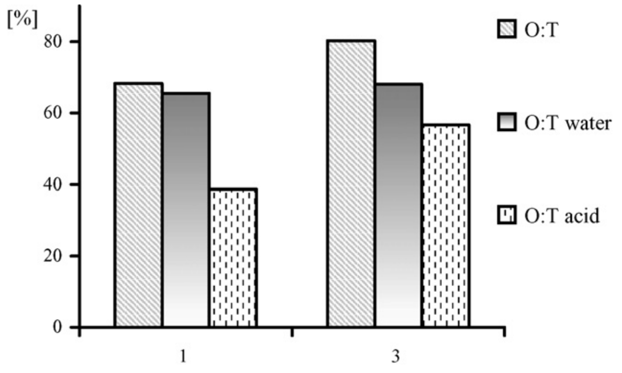


Fig. 3. Relative contents of non-degraded *N*-dodecylpyridine-3-carboxamide **1** and *N,N*-dihexylpyridine-3-carboxamide **3**, dissolved in a mixture of octane–toluene (4:1, v/v) with 5% addition of water or hydrochloric acid (4 M), after 10 h photodegradation (UV–vis, argon).

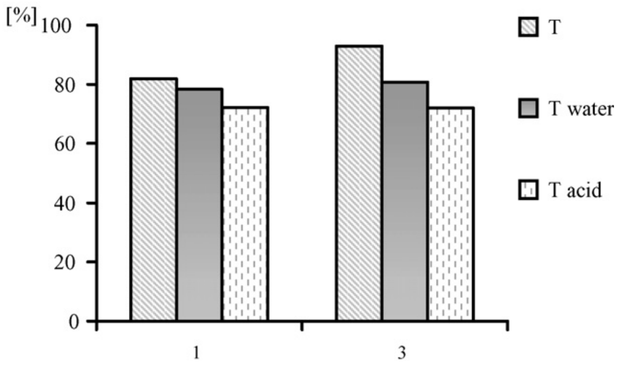


Fig. 4. Relative contents of non-degraded *N*-dodecylpyridine-3-carboxamide **1** and *N,N*-dihexylpyridine-3-carboxamide **3**, dissolved in toluene with 5% addition of water or hydrochloric acid (4 M), after 10 h photodegradation (UV–vis, argon).

tion degradation was the highest (Fig. 1). Similar results were obtained for other amides.

The decrease of the photodegradation degree in the toluene solution was due to the absorption of UV light by the aromatic solvent. Even 20% presence of toluene in the octane solution changed the rate of photodegradation from 91.9% (for octane) to 12.8% (for a mixture of octane–toluene (4:1, v/v)) after 3 h exposure. Also, the interaction between solvent and dissolved substance plays an important role; more so when as a solvent toluene is used rather than octane.

The degree of degradation of amides depended on the structure and number of alkyl groups. The comparison of the amide photodegradation in the octane–toluene solution indicated that amides with the *N*,*N*-dialkyl group are more stable (Fig. 2). Similar correlations were observed in the toluene solution.

The photostability of amides is higher for compounds containing a shorter carbon chain; amide with 2-ethylhexyl groups degraded the quickest. The susceptibility of *N*-(2-ethylhexyl)pyridine-3-carboxamide to degradation is the cause of the fragmentation at the tertiary atom carbon. Also, the 5% addition of water or hydrochloric acid in the organic phase influenced the photostability of pyridinecarboxamides (Figs. 3 and 4). The bubbling of water and hydrochloric acid through the solutions enhanced the photodegradation of amides. The higher photodegradation was observed after irradiation of amides in a mixture of octane–toluene with HCl bubbling. The degree of the photodegradation also depended on the structure of the amides group. For the octane–toluene mixture with 5% addition of water (Fig. 5), the highest photostability was obtained for *N*,*N*-dibutylpyridine-3-carboxamide; the amides with the 2-ethylhexyl group are the most susceptible to light. The presence of hydrochloric acid caused the partial solubility of amides **4** and **6** in the water phase and therefore the degree of photodegradation for these amides was not determined. *N*-Dodecylpyridine-3-carboxamide is less stable than the amide with the *N*,*N*-dihexyl group (Fig. 6).

The comparison of the *N,N*-dihexylpyridine-3-carboxamide stability when UV–vis and vis light was used indicated the higher effect of UV–vis light in the system when argon or air was bubbling through the solution (Fig. 7). The presence of air accelerates the degradation of the amide, especially under UV–vis light exposure. For example, after 600 min UV–vis exposure, the content of amide in the presence of argon and air was 80.4% and 47.5%, respectively. The coincident influence of both fac-

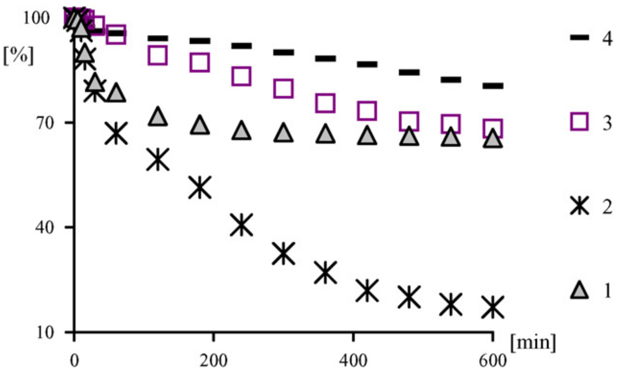


Fig. 5. Relative contents of non-degraded *N*-dodecylpyridine-3-carboxamide **1**, *N*-(2-ethylhexyl)pyridine-3-carboxamide **2**, *N,N*-dihexylpyridine-3-carboxamide **3**, *N,N*-dibutylpyridine-3-carboxamide **4**, dissolved in an octane–toluene mixture with 5% addition of water, during photodegradation (UV–vis, argon).

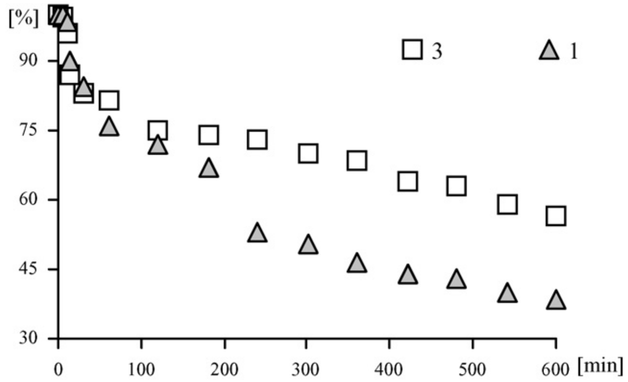


Fig. 6. Relative contents of non-degraded *N*-dodecylpyridine-3-carboxamide **1**, *N,N*-dihexylpyridine-3-carboxamide **3**, dissolved in an octane–toluene mixture with 5% addition of hydrochloric acid (4 M), during photodegradation (UV–vis, argon).

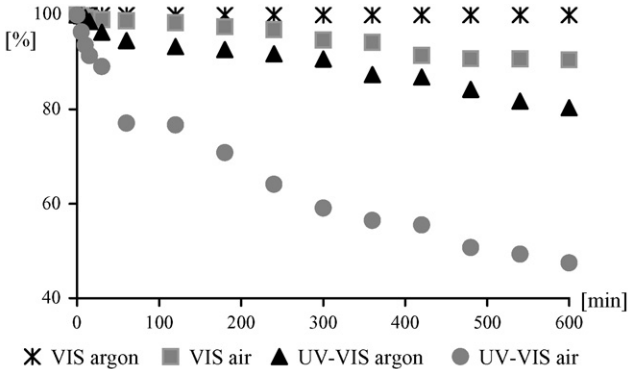


Fig. 7. Relative contents of non-degraded *N,N*-dihexylpyridine-3-carboxamide, dissolved in a mixture of octane:toluene (4:1, v/v), during photodegradation (UV–vis, vis, argon, air).

tors (UV light and air) could facilitate the formation of radical and accelerate amide degradation.

Also, the presence of air is the important factor of the amide degradation under exposure to vis light. For example, after 600 min exposure to light, the content of amide in the system with argon bubbling was nearly100%, and 90.5% in the system with air. The bubbling of air through the solution containing amide without light exposure did not degrade the amide.

HPLC/MS/UV, FT/IR and GC/MS analysis showed that the influence of light caused the formation of the photodegradation products and photosubstitution (Scheme 1).

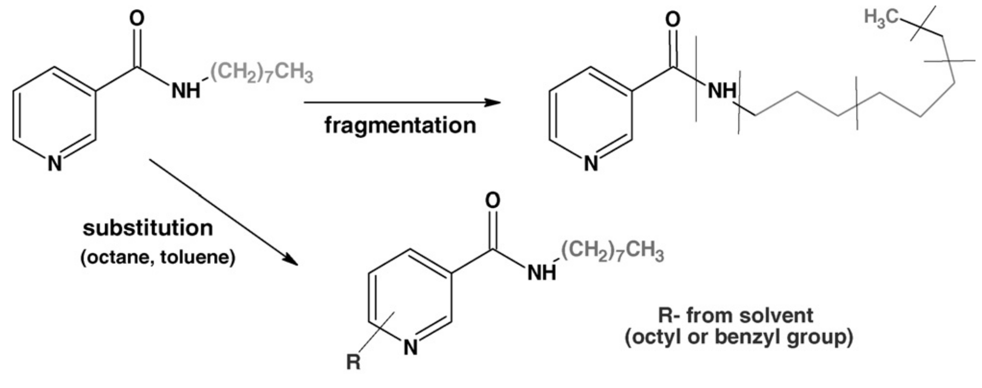
The photosubstitution products are amides containing the benzyl (peaks 6 in Fig. 8) or octyl (peaks 1–5 in Fig. 8) groups originated from solvent. The reaction of photosubstitution could be initiated by hydrogen abstraction from the solvent by n-Π^* or Π–Π^* excited state of the pyridine ring and n-Π^* of the carbonyl group [13]. Also the products of photosubstitution by the shorter carbon chain (C_2–C_4) were detected, though in minimal amounts. Similar photoreactions we observed during studies of the pyridinecarboxylates, where photosubstitution products were also observed [10].

The photodegradation of pyridine-3-carboxamides in a mixture of octane–toluene were compared with results obtained for pyridine-2-carboxamides (Fig. 9). Pyridine-2-carboxamides degraded quicker than pyridine-3-carboxamides. For example, *N*-dodecylpyridine-3-carboxamide after 10 h irradiation degraded by 32%, but pyridine-2-carboxamide with the same amide group degraded by 55%. The Π-deficient heterocyclic system exerts a significant electron-withdrawing effect on the carbonyl group at the two-position and consequently degradation of the amide group is easier at the two-position.

The comparison of photodegradation of esters and amides indicated that amides are more stable than esters with a similar structure. Esters and amides with the 2-ethylhexyl groups are the most sensitive on exposure to light, though 2-ethylhexyl ester degraded quicker, but all tested derivatives of pyridinecarboxylic acids are more stable than hydroxyoximes extractants (Fig. 10).

During UV–vis irradiation of copper complexes of amides the formation of a copper mirror on the optical filters was observed. This probably means that the electron transfer from the pyridinecarboxamide to the coordinated copper(II) ions took place yielding carboxyoxy radicals and copper(I). The carboxyoxy radicals decarboxylated to form pyridyl radicals, which reduced copper(I) to copper(0) [14].

The metal ion may have a different effect on photoreaction depending on the kind of coordination by an organic ligand. The photostability of copper complexes of amides of pyridine-3-carboxylic acid obtained in the excess of ligand (ligand:copper 20:1; Cu1 and Cu3 complexes) and in the excess of copper (ligand:copper 1:5; Cu2 and Cu4 complexes) were studied



Scheme 1.

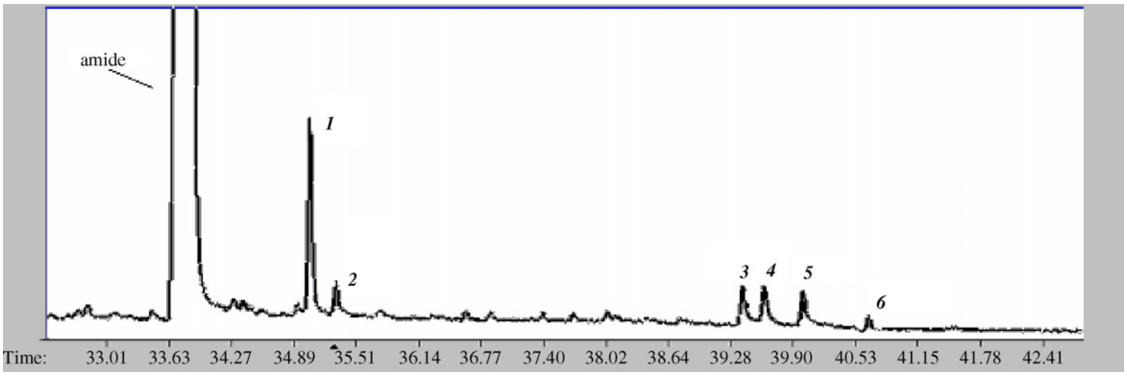


Fig. 8. The GC/MS chromatogram *N*,*N*-dihexylpyridine-3-carboxamide in an octane–toluene solution containing degraded amides and their by-products of photo-substitution (1–5 with octyl group and 6 with benzyl group) after 3 h of degradation by UV–vis light in an argon atmosphere.

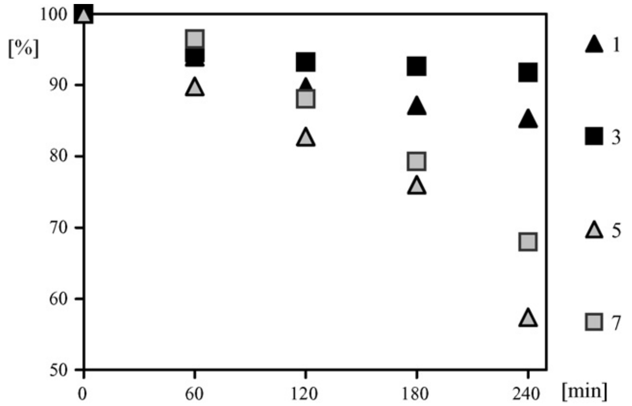


Fig. 9. Relative contents of non-degraded: *N*-dodecylpyridine-3-carboxamide **1**, *N*,*N*-dihexylpyridine-3-carboxamide **3**, *N*-dodecylpyridine-2-carboxamide **5** and *N*,*N*-dihexylpyridine-2-carboxamide **7**, dissolved in a mixture of octane–toluene (4:1, v/v), during photodegradation (UV–vis, argon).

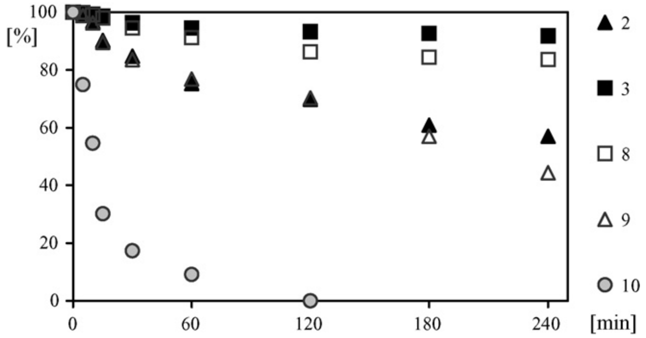


Fig. 10. Relative content of non-degraded: *N*-(2-ethylhexyl)pyridine-3-carboxamide **2**, *N*,*N*-dihexylpyridine-3-carboxamide **3**, octyl pyridine-3-carboxylate **8**, 2-ethylhexyl pyridine-3-carboxylate **9** and 2-hydroxy-5-*t*-octylacetophenone oxime **10**, dissolved in a mixture of octane–toluene (4:1, v/v) (UV–vis, argon).

(Tables 2 and 3; Fig. 10). A comparison of the obtained results of the photodegradation indicated that the presence of chloride and copper ions influenced the rate of photodegradation. The pyridine derivatives, in the presence of their copper complexes, degraded quicker than the free extractant. The copper complexes obtained in the excess of ligand (Cu1 and Cu3) had the molar ratio ligand:copper:chloride 2:1:2 or 3:1:2. When the copper to ligand ratio is higher than 5:1, amide extractant could create

Table 2
Photostability of amides of pyridine-3-carboxylic acid in toluene and in toluene containing their complexes with copper(II) under exposition of UV–vis light

Extractant or its complex	Complex composition [L:Cu:Cl]	Time of UV–vis light exposure [min]					
		0	30	60	120	180	240
		Content of amide (%)					
N,*N*-Dihexylpyridine-3-carboxamide		100	99.8	99.7	99.7	99.3	98.9
Complex Cu1	2:1:2; 3:1:2	100	96.5	90.3	88.4	86.3	84.7
Complex Cu2	1:1:2	100	98.2	93.8	91.7	86.3	79.1
Complex Cu3	2:1:2 and 3:1:2	100	93.9	88.4	84.3	82.7	80.1
Complex Cu4	1:1:2	100	97.1	95.7	82.8	85.1	78.7
N,*N*-dibutylpyridine-3-carboxamide		100	97.2	95.9	95.6	94.0	93.5
Complex Cu1	3:1:2	100	96.1	93.7	90.2	88.8	87.9
Complex Cu2	1:1:2	100	93.5	89.3	84.7	82.5	81.1
Complex Cu3	3:1:2	100	97.0	96.2	94.8	93.9	93.1
Complex Cu4	1:1:2	100	85.4	80.4	75.8	70.8	69.2
N-(2-Ethylhexyl)-pyridine-3-carboxamide		100	97.8	97.0	96.5	93.4	91.9
Complex Cu1	2:1:2; 3:1:2	100	99.8	96.8	95.1	87.1	82.6
Complex Cu3	2:1:2; 3:1:2	100	96.2	94.7	85.9	80.0	79.1

Table 3
Photostability of amides of pyridine-3-carboxylic acid in an octane–toluene solution and in an octane–toluene solution containing their complexes with copper(II) under exposition of UV–vis light

Extractant or its complex	Complex composition [L:Cu:Cl]	Time of UV–vis light exposure [min]					
		0	30	60	120	180	240
		Content of amide (%)					
N,*N*-Dihexylpyridine-3-carboxamide		100	96.3	94.6	93.3	92.7	91.8
Complex Cu1	2:1:2 and 3:1:2	100	90.1	86.1	83.0	81.1	75.4
Complex Cu2	1:1:2	100	77.0	71.2	67.5	60.7	52.0
Complex Cu3	2:1:2 and 3:1:2	100	88.6	85.6	82.8	79.1	74.2
Complex Cu4	1:1:2	100	61.0	56.6	54.4	52.8	51.5
N,*N*-Dibutylpyridine-3-carboxamide		100	98.7	98.6	98.0	96.7	95.9
Complex Cu1	3:1:2	100	95.3	93.0	87.7	84.1	77.1
Complex Cu2	1:1:2	100	88.8	80.7	73.5	60.7	66.1
Complex Cu3	3:1:2	100	96.2	95.6	88.8	84.1	76.6
Complex Cu4	1:1:2	100	91.0	86.5	84.9	72.0	63.9
N-(2-Ethylhexyl)-pyridine-3-carboxamide		100	84.8	75.3	69.8	60.9	57.1
Complex Cu1	2:1:2 and 3:1:2	100	90.1	89.2	83.3	78.5	74.6
Complex Cu3	2:1:2 and 3:1:2	100	89.2	84.4	81.0	73.1	67.7

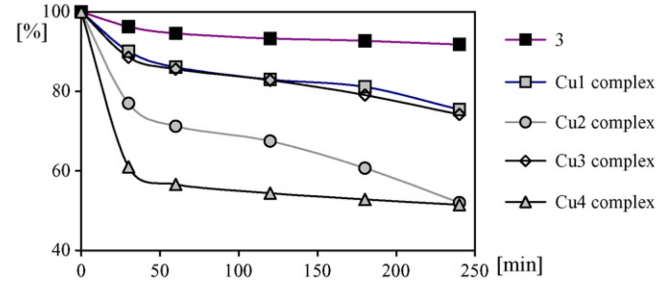


Fig. 11. Photostability of *N*,*N*-dihexylpyridine-3-carboxamide **3** in toluene and toluene solutions containing their complexes with copper(II) (UV–vis, argon).

the complex 1:1:2. The content of copper in the organic phase of Cu2 and Cu4 after extraction indicated the presence of all copper complexes (Fig. 11).

For systems containing copper complexes, where the molar ratio of ligand to copper was 2:1 or 3:1, the increase of chloride ions concentration did not affect the degree of photodegradation. But the presence of copper complexes 1:1:2, where the molar ratio of ligand to copper was 1:1, in the mixture of complexes, caused significant change in the stability of ligand. The increase of the chloride ions concentration enhanced the rate of photodegradation for Cu2 and Cu4 complexes.

4. Conclusions

The obtained results indicated the influence of light (UV and vis) on the stability of pyridinecarboxamides. The degree of the photodegradation depended on the type of solvent and presence of air. The least degree of photodegradation was observed in toluene solutions. Photodegradation occurred slightly faster in the mixture of octane–toluene, and degradation was the highest in the octane solutions. The bubbling of water, hydrochloric acid or air through the solutions enhanced the photodegradation of extractant. Even in the system, where vis light was used, the influence of air was considerable. Thus, one can expect a degradation of pyridinecarboxamide as the extractant both during extraction and stripping carried out in extraction installations with open mixers and settlers, where the exposure of light is unavoidable.

The degree of degradation of amides depended on the structure and number of alkyl groups. The *N*,*N*-dialkylamides are more stable than *N*-alkylamides. The photostability of amides is higher for compounds containing shorter carbon chains, but amide with 2-ethylhexyl groups degraded the quickest. Also, the position of the amide group at the pyridine ring influenced the rate of photoreaction; pyridine-2-carboxamide degraded quicker than pyridine-3-carboxamide with the same amides group.

HPLC/MS/UV, FT/IR and GC/MS analysis showed that the influence of light caused the formation of the photodegradation products of the amide group and photosubstitution at the pyridine ring.

The analysis of the influence of ions of copper(II) and chloride during the photodegradation of copper complexes with pyridinecarboxamide indicated that the copper complexes, in which the molar ratio of ligand to copper was 1:1, caused a significant change in the ligand stability. The increase of the chloride ions concentration enhanced the rate of the pyridinecarboxamide photodegradation.

Pyridinecarboxamides are more stable against UV–vis light than esters of pyridinecarboxylic acid, but both tested derivatives of pyridinecarboxylic acid are more stable than hydroxyoximes extractant.

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